

## APPENDIX E TO PART 50 [RESERVED]

## APPENDIX F TO PART 50—MEASUREMENT PRINCIPLE AND CALIBRATION PROCEDURE FOR THE MEASUREMENT OF NITROGEN DIOXIDE IN THE ATMOSPHERE (GAS PHASE CHEMILUMINESCENCE)

## PRINCIPLE AND APPLICABILITY

1. Atmospheric concentrations of nitrogen dioxide (NO<sub>2</sub>) are measured indirectly by photometrically measuring the light intensity, at wavelengths greater than 600 nanometers, resulting from the chemiluminescent reaction of nitric oxide (NO) with ozone (O<sub>3</sub>). (1,2,3) NO<sub>2</sub> is first quantitatively reduced to NO(4,5,6) by means of a converter. NO, which commonly exists in ambient air together with NO<sub>2</sub>, passes through the converter unchanged causing a resultant total NO<sub>x</sub> concentration equal to NO+NO<sub>2</sub>. A sample of the input air is also measured without having passed through the converter. This latter NO measurement is subtracted from the former measurement (NO+NO<sub>2</sub>) to yield the final NO<sub>2</sub> measurement. The NO and NO+NO<sub>2</sub> measurements may be made concurrently with dual systems, or cyclically with the same system provided the cycle time does not exceed 1 minute.

## 2. Sampling considerations.

2.1 Chemiluminescence NO/NO<sub>x</sub>/NO<sub>2</sub> analyzers will respond to other nitrogen containing compounds, such as peroxyacetyl nitrate (PAN), which might be reduced to NO in the thermal converter. (7) Atmospheric concentrations of these potential interferences are generally low relative to NO<sub>2</sub> and valid NO<sub>2</sub> measurements may be obtained. In certain geographical areas, where the concentration of these potential interferences is known or suspected to be high relative to NO<sub>2</sub>, the use of an equivalent method for the measurement of NO<sub>2</sub> is recommended.

2.2 The use of integrating flasks on the sample inlet line of chemiluminescence NO/NO<sub>x</sub>/NO<sub>2</sub> analyzers is optional and left to the discretion of the user or the manufacturer. Use of the filter should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particulates. Users are cautioned that particulate matter concentrated on a filter may cause erroneous NO<sub>2</sub> measurements and therefore filters should be changed frequently.

2.3 The use of particulate filters on the sample inlet line of chemiluminescence NO/NO<sub>x</sub>/NO<sub>2</sub> analyzers is optional and left to the discretion of the user or the manufacturer. Use of the filter should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particulates. Users are cautioned that particulate matter concentrated on a filter may cause erroneous NO<sub>2</sub> measurements and therefore filters should be changed frequently.

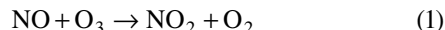
3. An analyzer based on this principle will be considered a reference method only if it has been designated as a reference method in accordance with part 53 of this chapter.

## CALIBRATION

1. *Alternative A*—Gas phase titration (GPT) of an NO standard with O<sub>3</sub>.

*Major equipment required:* Stable O<sub>3</sub> generator. Chemiluminescence NO/NO<sub>x</sub>/NO<sub>2</sub> analyzer with strip chart recorder(s). NO concentration standard.

1.1 *Principle.* This calibration technique is based upon the rapid gas phase reaction between NO and O<sub>3</sub> to produce stoichiometric quantities of NO<sub>2</sub> in accordance with the following equation: (8)



The quantitative nature of this reaction is such that when the NO concentration is known, the concentration of NO<sub>2</sub> can be determined. Ozone is added to excess NO in a dynamic calibration system, and the NO channel of the chemiluminescence NO/NO<sub>x</sub>/NO<sub>2</sub> analyzer is used as an indicator of changes in NO concentration. Upon the addition of O<sub>3</sub>, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of NO<sub>2</sub> produced. The amount of NO<sub>2</sub> generated may be varied by adding variable amounts of O<sub>3</sub> from a stable uncalibrated O<sub>3</sub> generator. (9)

1.2 *Apparatus.* Figure 1, a schematic of a typical GPT apparatus, shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the O<sub>3</sub> generator should be of glass, Teflon®, or other non-reactive material.

1.2.1 *Air flow controllers.* Devices capable of maintaining constant air flows within ±2% of the required flowrate.

1.2.2 *NO flow controller.* A device capable of maintaining constant NO flows within ±2% of the required flowrate. Component parts in contact with the NO should be of a non-reactive material.

1.2.3 *Air flowmeters.* Calibrated flowmeters capable of measuring and monitoring air flowrates with an accuracy of ±2% of the measured flowrate.

1.2.4 *NO flowmeter.* A calibrated flowmeter capable of measuring and monitoring NO flowrates with an accuracy of ±2% of the measured flowrate. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

1.2.5 *Pressure regulator for standard NO cylinder.* This regulator must have a nonreactive diaphragm and internal parts and a suitable delivery pressure.

1.2.6 *Ozone generator.* The generator must be capable of generating sufficient and stable levels of O<sub>3</sub> for reaction with NO to generate